6.0 Computationally-Driven Materials Development

Computationally-based materials design and manufacture were envisioned in the earliest days of quantum mechanics. Implementation awaited the advent of modern computers. Only now are we on the threshold of a modeling era that pervades the materials fields. This is not merely the application of computers to existing materials technologies and equipment automation, but rather using computers to change the way materials problems are approached.

In the new paradigm modeling will be integrated throughout the materials sciences and often applied by the modeling non-specialist. For example, before performing traditional experiments, the organic chemist of the future regularly will execute a series of computational experiments. Physical experiments will often be more focused and defined, and sometimes no physical experiments will be needed to obtain required information. The same will hold true for many of the phases of materials development.

More efficient development of new materials, better control and improved properties in known materials, more environmentally friendly synthetic schemes, improved opportunities for meeting multiple requirements, substantially improved understanding of materials, dramatic reductions in resources expended on unproductive materials R&D avenues, improved quality control and lower costs in manufacturing, and more precise troubleshooting of future problems can be expected from this revolution. Inasmuch as materials are often the critical limiters in AF systems, the impacts to be realized are broad. The AF must nurture these changes.

Materials modeling is enormously complex. The scheme illustrated in Figure 6.1 summarizes the hierarchical and interdisciplinary natures of materials development. At the left of Figure 6.1 are depicted the atomistic models, including first principles quantum mechanical methods. Progressing up the chain to finite element methods, one is less concerned about atomic details and more concerned about bulk properties. The next stages include the realm of modeling processes, and ultimately system modeling, which is beyond the scope of this report. For a new material to go from a laboratory curiosity to an engineering material, the entire spectrum must be spanned. This journey can require 20-50 years, substantially longer than the plant design analogy cited above. Computationally driven materials development encompasses all the phases in Figure 6.1, and is changing the practices of the disciplines shown at the bottom of Figure 6.1 as they relate to materials development.

In materials sciences only limited specific applications of materials modeling are currently in use. While examples of multimillion dollar corporate decisions based on molecular simulations exist, revolutionary change is still on the horizon. Two requisites to induce this revolution are 1) broad based computer simulations as reliable as experiments, and 2) acceptance by the practicing community of the results from such techniques. The latter entails a cultural change which will occur as the methods prove themselves. Whereas theoretical results competing with experimental findings are not uncommon in certain fields of physics and mechanics, this is generally not the culture in materials development. In the materials sciences, simulations that can challenge experimental findings have been rare. The focus should then be on “What bottlenecks are inhibiting such a revolution in materials sciences?”

The greatest limiting factor in modeling has traditionally been computer power, but this is often no longer the case. Even the higher-end personal computers are capable of modeling

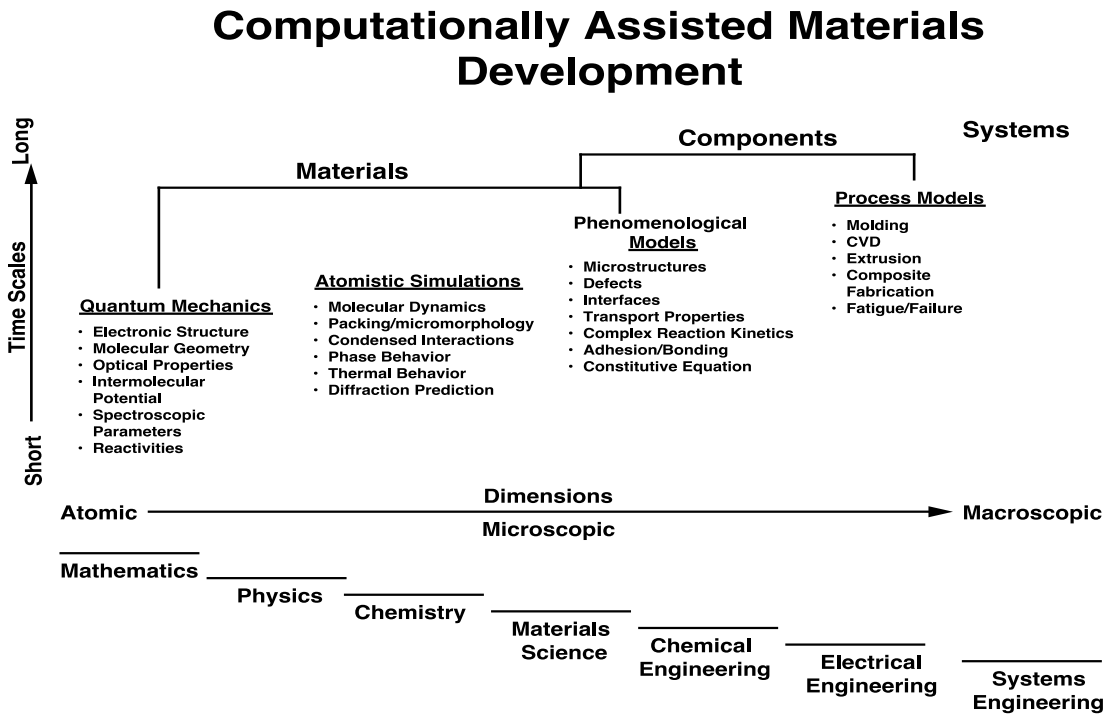

Figure 6.1 Computational Assisted Materials Development

problems that a few years ago were reserved for mainframe and supercomputers. This is not to say there isn't a place for large computers. Many computationally-limited problems exist, but the trend is clearly toward high-end workstations at the desktop. The advances in computer technologies and falling computer price/performance ratios will continue and facilitate application of modeling methods at the desktop. The workstation at the desktop will be particularly useful for the materials scientist for synthesis as well as being useful for prediction of properties and behavior.

Increasingly, software is more limiting than hardware. Software modernization is a concern. Significant programming advances, such as current efforts in massive parallelization, seem to be funded, at least while the techniques are new, revolutionary, and offer dramatic improvements. But more evolutionary software enhancements are lagging in their implementation into codes. To understand this we consider typical transition paths.

Most materials codes originate in academic laboratories and are either directly distributed to other researchers or are commercialized. Academic researchers find it difficult to raise funds to revise old codes. Research funds are typically awarded for programming new and exciting things, not for optimizing integral evaluation and other routines first developed 25 years ago. Likewise, computer scientists don't receive funds for incorporating newer programming methods into old software, but rather for developing new programming methods. The companies, for those codes that are commercialized often don't have the resources to devote to updating old

products. Hence, many codes have archaic, inefficient segments with no viable mechanism for rewriting old codes to take advantage of newer program technologies. Significant enhancements in applicability and capability could be realized with such modernizations. Complete rewrites are not needed, but rewriting the bottlenecks, memory or computationally inefficient and resource intensive routines would be beneficial.

The most important and numerous advances are yet to be made in coding property calculations and in method development. Often one is interested in a property or process for which no adequate software exists. This may be a matter of the software not having been written, but more often the underlying theoretical methods to calculate such properties simply don't exist. The theory hasn't been reduced to programmable logic. In these areas the Air Force can provide direction and leadership by investing in areas where software and methods are lacking but are needed for Air Force programs. Indeed, this leadership has been demonstrated. About 1989, none of the common first principle codes were capable of calculating nonlinear optical properties for molecules. At that time interest was generated from the Air Force in nonlinear optical materials research, and soon thereafter techniques were developed and implemented that could calculate some nonlinear optical properties. These codes are now broadly applied in academic, government, and industrial laboratories. Still, very little of the potential has been realized in other properties simulations.

Cross-discipline interaction is a must. The theoretical and modeling communities should address problems that span the spectrum of materials development. Certainly technique development, coding, and validation will remain the domain of the specialist and these must all be nurtured, but the utility to the non-specialist must also receive high priority. Too often the modeling results are in arcane terms, and are focused on modeling and theoretical minutiae. Cross-fertilization—true teaming—should be encouraged. One mechanism to encourage this interdisciplinarity, as now being implemented at one Air Force laboratory, is to not isolate modelers as separate groups, but rather to incorporate them into the overall research teams. This has the advantage of focusing the modelers on specific problems, though it does run the danger of neglecting methods development, which often takes years. Too often modelers do not know the most important questions to address, while experimentalists are unaware of the capabilities and limitations of modeling.

Data fusion—incorporating information from lower level calculations to higher level users, experimental and modelers—promises to be a challenging problem. For example, some questions must be addressed at the atomistic or molecular level, but that degree of detail is neither needed nor desired at the higher level. If these linkage issues can be addressed, materials could be straightforwardly tailored to specific engineering applications.

The vision of this section of the overall report is to anticipate what areas the Air Force should emphasize and what relationships the Air Force should foster. For technical emphasis, the criterion should be to support those modeling techniques that are key to critical Air Force materials technologies. Several areas for emphasis are discussed below.

6.1 Propellants and High Energy Materials

There has been and continues to be much modeling effort in this technology area. The modeling has been focused on designing new materials; however, there is not enough cross-disciplinary interaction. Modeling areas to be emphasized are 1) solvent and chemical environment interactions with high energy molecules, 2) improved methods of mapping out reactions, and 3) methods to model and understand kinetics in multiphase systems. There is much effort in the quantum field addressing solvent interactions, so this needs sustained emphasis and incorporation into the energetic materials efforts. Discovering unusual reactivities, especially by modeling techniques, is a wide open field. Perhaps high energetic materials is an ideal place to emphasize and develop methods for this. The actual experiments are difficult, dangerous, and often ambiguous. Since many of the molecules are small to moderate size, some advanced, experimentally competitive techniques are quite applicable. What is lacking is a reliable technique that can quickly and efficiently generate reaction paths. This is a daunting task, and will require long term support. Since reactivities, especially in propellants, often depend critically on grain size and processing parameters, incorporating these factors into models is critical.

6.2 Magnetic Materials

The importance of magnetic materials is noted elsewhere in this report. Molecular magnetics are relatively new, yet very little if any modern modeling has been done. The codes and techniques are scattered or are nonexistent. For example, there are no known codes that can calculate or estimate bulk magnetic susceptibilities for molecular magnetic compounds. Little is understood in how to design a molecular magnet. If modeling techniques were developed, they could provide the needed insight.

6.3 Epitaxial Growth Processes

Epitaxial processes underpin the electronics industries. These include chemical vapor deposition (CVD), which is used for the majority of established semiconductor thin film growth processes, and molecular beam epitaxy (MBE), which will be used to produce the next generation electronic and inorganic optical materials taking advantage of quantum effects. The most advanced simulations are of gas-phase materials, yet very little atomistic modeling has been applied to the relevant gas-phase processes in CVD. In MBE, there are no gas-phase interactions due to the ultrahigh vacuum environment; instead an understanding of surface processes and energetics on an atomic scale are of importance in establishing the growth conditions for high quality films. Some preliminary computational work has been done in this area but much more is needed. Additionally, organic based photonic and electronic materials are emerging technologies, and vapor deposition may play an important role. Again, the modeling could make a substantial contribution to the development of the materials processes. Note that modeling could be employed virtually from the ground up for electronic and nonlinear optical materials. Early attempts at this philosophy have been initiated for inorganics, but organic materials should also be well suited to this approach.

6.4 Materials Level Modeling

Great strides are being made in modeling the behavior of composite materials, for example in understanding weaknesses induced by holes. This is a critical area to the Air Force,

because of the lack of civilian leadership in this area. The field has a history of highly empirical models with expensive experiments required to even parameterize the computer models. This is changing; better deterministic, hence more predictive, models (rather than parametric fits of experimental data) are forthcoming. Other areas, such as a priori prediction of matrix-reinforcement interface properties, are still distant, and so are methods in other composite materials areas. However, this is a critical technology to the Air Force, and support of it must continue. With the downsizing of the industrial base, the cohesiveness and coordination is centered about the Air Force laboratories. The savings and capabilities of future systems stand to benefit greatly from this work.

6.5 Ceramics, Alloys, Intermetallic Compounds, and Interfaces

Atomistic simulations are not well advanced for these systems. For ceramics, alloys, intermetallics, and interfaces, the modeling situation is not even close to the level of sophistication and application of the organic materials. New techniques, such as the density functional methods, are being pursued, but much remains to be done. Very few dynamic properties can be modeled, and often the models are highly simplified and parameterized. What this field requires is sustained effort in general, and for the Air Force leaders to give focus on important areas.

6.6 Photochemical Modeling

In the relatively short term—five years—the ability to model excited-state and photochemical properties from first principles will mushroom. Relatively little detail is known about excited state structures and reactivities. Indeed, it is almost impossible to get this information experimentally. Most synthetic chemists will avoid photochemical processes if possible, since such processes are difficult to control. Much of this difficulty may stem from the lack of detailed understanding in the field.

In the near term, modeling may start to change this status. While practical applications will be further out, the possibilities are exciting. For example, the same excited states and reactive species often play roles in degradation processes such as stress-induced reactions or photochemical degradation. Modeling may realistically be capable of addressing the problems and lead to materials solutions to chronic maintenance problems. One possibility is designing materials to give readily detectable signals when failure or degradation occurs. Another potential area is the use of holographic masking and photo-assisted reaction schemes for semiconductor thin films. These procedures could lead to an increased integration of different components on the same chip, and may even largely replace expensive processing steps, such as traditional masking and photolithography. This would result in substantial gains in capabilities at reduced cost.

6.7 Bulk Properties

Data fusion—linking of lower-level data, experimental, theoretical, or both, into calculation of engineering properties of interest—is a key component in computationally-driven materials development. For example, how do the coefficient of thermal expansion (CTE), dielectric constants, thermal characteristics, and interfacial behavior vary with chemical composition or processing conditions? While many of these may not be calculable in the near term, specific

properties and behavior will succumb to modeling. There is effort to link quantum mechanics with molecular mechanics, but much remains to be done. Cross-discipline efforts should be fostered.

6.8 Defects, Dynamic Behavior and Transport Properties

In many materials, either the interesting properties or the limiting behaviors are dominated by defects. The easy problems in modeling are to handle defect free, ideal materials. That is valuable for both understanding and predicting ultimate properties. However, increased emphasis is needed for defect modeling. Some defects, such as charge carriers in organic conductors, are amenable to current methods. Others, particularly when intermolecular interactions and dynamic behavior are key components, are much less advanced. This is particularly true when dynamic electronic behavior is involved. Dynamics based on computational fluid dynamics (CFD) continuum models or molecular dynamics (i.e. sophisticated ball and spring) atomistic models are well developed. Only now is time-dependent electronic behavior being addressed. Here, computer power is highly limiting and efficient codes are sorely lacking.

6.9 Synthesis and Reactivities, Synthetic Paths

Pioneering work has been done in modeling the synthesis of organic materials, particularly the famous retrosynthetic schemes. Much of this effort has been driven by the pharmaceutical industry. Modeling reaction conditions, synthetic paths, and reaction catalogs are lacking for other classes of materials—intermetallics, ceramics, alloys and polymers. Great benefit can be derived from more effort here. It can be experimentally tedious to determine mechanistic details, and yet these details are necessary for optimizing reaction and processing conditions.

6.10 Atomistic Catalyst Modeling

Our society relies upon catalysts. The quest for efficient, cheap, reliable catalysts is common to almost all chemical development. This area is fraught with difficulty, in that catalytic activity depends upon many parameters. Not surprisingly, modeling in this area is driven by particular industries, especially the petrochemical industry. No government nurturing seems needed there. However, in areas of Air Force interest, such as propellant manufacture or catalysts for curing composites, application of existing or new modeling tools could facilitate the development of lower-cost processes.

6.11 Modeling Heterogeneous Materials

Atomistic and continuum models are focused on homogeneous materials. As discussed above, defects are beginning to be modeled. What is virtually neglected is heterogeneous materials. Simply put, the methods used for modeling organic molecules are quite different from those used to model intermetallic compounds, ceramics, or glasses. This is understandable, since the bonding in organic molecules, inorganics, glasses, metals, and ceramics differ. Further, hybrid materials have emerged with new and revolutionary properties. Much remains to be done here, especially in understanding interfacial behavior, predicting and designing interfacial behavior, and the a priori prediction of phase transitions and degradations.

6.12 Advanced Synthesis and Processing

Spectacular strides have been achieved in recent years in the pharmaceutical industry toward automation of drug discovery. Combinatorial chemistry is the term used to describe efficient, highly automated methods in which tens of thousands of compounds are synthesized and tested for pharmaceutical activity in short times. Certainly this is possible with peptides since peptide synthesis is a well understood, defined chemical process. These techniques might also be applicable to the less well defined areas. One distinct possibility is in alloy testing. Again, some of the synthetic automation techniques and logic for testing large numbers of samples could be applied to quickly optimize alloy composition for specific applications. Overlapping with robotics applications, emphasis should be placed on automating well defined chemical and processing steps. While this is done on the industrial scale, little has been done in automation for materials development. An achievable goal would be automated synthesis for materials screening on a broad basis.

6.13 Solid State Materials

Out of the possible solid-state materials, only a few have found technical application. Indeed, until recently solid-state physics has not been emphasized in the U.S., and technological leadership has come from Europe and Japan. Beginning in the 1980s, the NSF recognized this cultural shortcoming, and increased its emphasis in this area of materials science. Modeling in solid-state physics, with the exception of modeling simple metals and semiconductors, is relatively unadvanced. Part of the difficulty arises in that many engineering properties depend upon particle size and processing conditions, which tend to be material specific. Given the range of possible materials and applications, sophisticated (i.e., beyond the Huckel independent electron model) methods should be brought to bear. Likely techniques will be applicable from other areas, but the Air Force can provide leadership in areas and topics of interest.

Solid-state theoreticians are continuing to develop full-range computer codes that can treat an almost limitless variety of semiconductor combinations, and which have the predictive power to model several physical phenomena: absorption, lifetime, mobility, third-order nonlinear susceptibility of quantum wires, to name a few. At present, these models continue to be specific to the materials and device of interest. In the future, these models need to become more universal, so that there are not separate models for each combination of semiconductor multilayers such as Si/SiGe or GaAs/GaInP. Another challenge of modeling in the future will be in the areas of lower dimensional structures, quantum wires and dots, and superlattices involving new materials combinations. As the complexity of the layered material designs continues to grow beyond simple two-layer heterostructures, the models predicting the properties of these materials will also have to advance. In particular, the area of quantum electronics continues to spawn new or improved device concepts for devices from infrared detectors to laser diodes, whose properties will continue to challenge modelers for a long time into the future.

6.14 Summary

In summary, computer-driven materials development is not directed toward a specific system, but toward materials technology. Materials is a pervasive technology, and the advances outlined above will lead to dramatic changes in the entire enterprise. As such, the Air Force has

a keen interest in nurturing these developments, incorporating them into its internal and extramural programs, and leading the modeling technology in selected areas while leveraging off-the-shelf technologies as they become available. Unlike most revolutions, this one is slow in coming, but it is nevertheless very real. It portends dramatic changes in how materials will be developed and emphasizes the efficient use of resource dollars. Ultimately, materials and processes must be translated from the computer to the real world.